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(54) Title: SUNSCREENS AND COMPOSITIONS CONTAINING THEM (57) Abstract A sunscreen agent which is a non-dye, substantially non-fluorescent, non-quaternary ammonium compound which absorbs UVA and/or UVB radiation wherein at least 5 %, preferably at least 7.5 %, more preferably at least 10 % by weight of the agent is deposited on a sheet of cotton-fabric immersed in a solution of 0.2 g/l of said agent in water for 1 hour at 21 °C at a solution:sheet weight ratio of 25:1, (preferably followed by rinsing) and then followed by drying.		

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- 1 -

SUNSCREENS AND COMPOSITIONS CONTAINING THEM**5 Technical Field**

The present invention relates to detergent compositions that enhance the UV barrier provided by fabric, which in some cases, mitigates dye transfer between fabrics and which can protect fabric from photofading. It also relates to specific sunscreen agents
10 which give this capability to the compositions.

Background of the Invention

The colour of fabrics can be altered during the laundering process or during wear or use
15 by sun fading.

The fading of coloured fabrics by sunlight during wear and during drying is a major problem for consumers. Sun fading of fabrics is of specific concern to consumers because the contrast between exposed and unexposed areas makes it particularly
20 noticeable. e.g on collars, inside versus outside of garments, and on wrap around garments such as saris.

In addition consumers rely on the use of clothes to protect them from UV light. It is frequently beneficial to enhance the UV protection given by clothes, particularly light
25 weight garments worn in hot weather.

- 2 -

The use of certain sunscreens in fabric treatment has already been discussed in the literature. US-A-4 788 054, teaches the use of N-phenylphthalisomides as ultraviolet radiation absorbers for cotton, wool, polyester and rayon.

- 5 WO 96/03369 discloses the use of butylated hydroxy toluene for the protection of surfaces from physical and chemical degradation.

The use of particular sunscreens for the treatment of fabrics to increase the sun protection factor (SPF) is known from EP-A-728 749. Furthermore, the use of the
10 sunscreens including those of EP-A-728 749 in combination with dye transfer inhibiting polymers comprising one or more monomeric units containing at least one = N-C(=O) but not an -oxide group to mitigate dye fading between fabrics is known from our co-pending European application no. 97302965.5

- 15 However, conventional sunscreens are either substantially water-insoluble, rendering them difficult to deliver uniformly to the fabric during the wash, or else they are non-substantive to cotton, i.e. they fail to deposit on cotton garments.

One or both of the aforementioned problems can now be overcome by incorporating a
20 new form of sunscreen in the detergent composition. These new sunscreens, according to the present invention are agents which absorb UVA and/or UVB radiation, they are substantially non-dyeing and substantially non-fluorescent but are substantive to cotton.

- One sunscreen agent which potentially fulfils these criteria is N, N, N-trimethyl-4-
25 (2-oxoborne-3-ylidene-methyl)anilinium-methyl sulphate. This material is described in GB-A-1 387 520 and is available commercially as Mexoryl SO (Trade Mark) ex. Chimex. However, being a quaternary ammonium compound, it is capable of

- 3 -

complexing with certain kinds of ingredient regularly found in detergent composition, e.g. anionic surfactant. Such complexing could render the material incapable of effective deposition on the fabric from washes containing typical surfactant levels.

5 Definition of the Invention

Thus, in one aspect, the present invention now provides a sunscreen agent which is a non-dye, substantially non-fluorescent, non-quaternary ammonium compound which absorbs UVA and/or UVB radiation wherein at least 5% by weight of the agent is
10 deposited on a sheet of cotton-fabric immersed in a solution of 0.2 g/l of said agent in water for 1 hour at 21°C at a solution:sheet weight ratio of 25:1, (preferably followed by rinsing) and then followed by drying.

In colour chemistry, the verb "to dye" is often understood to mean "to be taken-up by
15 the fabric" and so "non-dyeing" would sometimes be interpreted as "non-absorbing". For the avoidance of doubt, is used herein, the term "to dye" means "to colour" and "non-dyeing" and "non-dye" mean "non-colouring" and "non-colourant" respectively. Moreover, all references to colouring include any form of staining and so non-colouring implies non-staining.

20

Preferably, the sunscreen agent is of the general formula (I) or general formula (III) below.

As well as having the aforementioned sunscreen property, at least some agents
25 according to the present invention may also inhibit dye transfer. During the laundering process there is a tendency for coloured fabrics to release dye into the wash solution. This is a most persistent and troublesome problem as this released dye can then be

- 4 -

transferred onto other fabrics or other parts of the same garment. In order to mitigate dye transfer between fabric articles during a wash cycle it is conventional for dye transfer inhibiting polymers to be included in detergent compositions where such an inhibition effect is desired.

5

Detailed Description of the Invention

Sunscreen Agent

10 Sunscreen agents according to the present invention may be chemically modified dyes or fluorescers, that is to say they are conventional dye or fluorescer materials whose chemical structure (in the case of dyes) has been modified so as not to dye the fabric at the concentration in which they are used in the wash liquor, or (in the case of fluorescers) to be substantially non-fluorescent.

15

Examples of dye types and fluorescers and their syntheses are given in "Color Chemistry, Synthesis Properties and Applications of Organic Dyes and Pigments," second and revised edition, by H Zollinger, published by VCH, 1991; in "The Chemistry of Synthetic Dyes", vol 3, by K Venkataraman, Academic Press, 1970; and
20 in "Modern Colorants Synthesis and Structure", edited by A T Peters and H S Freeman, published by Blackie academic and professional, 1995.

25

The synthetic procedures described in these books can be used to synthesise the substantive colourless dyes or non-fluorescent fluorescers which are agents according to the present invention. These agents therefore have dye-like or fluorescer-like structures with modified spectral properties.

- 5 -

For example coloured aluminium phthalocyanine sulphonates which are blue can be made colourless by adding additional groups and synthesising sulphonated naphthalocyanines which are colourless, absorb in the UV (and preferably the infra-red) and are substantive (e.g. see US-A-4 400 173).

5

Such dyes or fluorescers must also be modified so that their substantivity (i.e. ability to deposit and adhere) to cotton is not destroyed.

Despite being substantially non-dyeing, in some circumstances, at the use concentration, the agents according to the present invention may slightly alter the perceived hue of existing colours. Very preferably, they do not absorb radiation in the region of 400-700nm, although a limited amount of absorption within this range is permissible, provided that the substantially non-dyeing behaviour is maintained. Furthermore, being substantially non-fluorescent, agents according to the present invention preferably produce less than 40%, more preferably less than 25%, still more preferably less than 10%, most preferably less than 1% of the luminosity (total flux emission per unit area) as compared with the commercially available fluorescer Tinopal CBS-X (Trade Mark) when deposited on fabric in the same weight concentration per unit area.

20

Agents according to the present invention must also absorb UVA and/or UVB radiation. The International Commission on Illumination (CIE) in 1970 defined the ultraviolet radiation wavelength sub-divisions as follows:-

25

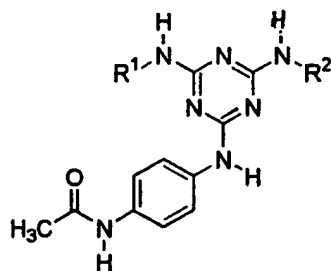
UVA	315-400nm
UVB	280-315nm
UVC	100-280nm

- 6 -

Preferably, an agent according to the present invention absorbs radiation over the wavelength range from about 200nm-450nm, more preferably from 200nm-400nm (e.g. from 280nm to 400nm) still more preferably from 200nm to about 350nm, most preferably from about 200nm to about 400nm, although the absorbency will inevitably be non-uniform over the range.

It is preferred if the sunscreen is a material which absorbs UV in both the UVA and the UVB region of the spectrum. It is further preferred if the sunscreen is capable of reducing the transmission of harmful UV rays through fabrics and thus increasing the ultraviolet protection factor of the fabric.

One advantageous class of sunscreens which may be used with composition of the invention have a structure corresponding to formula (I):



(I)

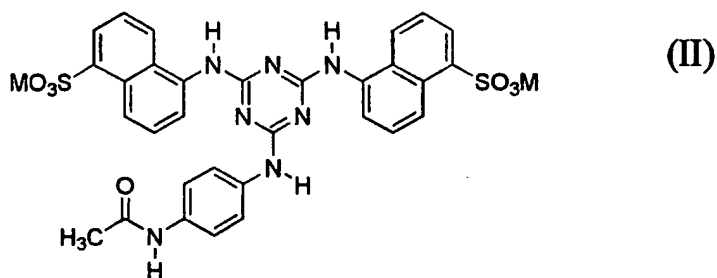
in which R¹ and R² are the same or different and are substantially flat planar groups which cause the molecule to absorb UVA and/or UVB, and have a water solubilising group. For example, R¹ and R² may be selected from aliphatic and/or aromatic

- 7 -

mono-, bi- or tricyclic groups optionally incorporating one or more heteroatoms and substituted by one or more water solubilising groups, e.g. selected from iodo, tertiary amino, sulphonic acid, carboxylic acid and nitro groups, or salt forms thereof.

A preferred example of a compound of formula (I) is a compound of formula (II)

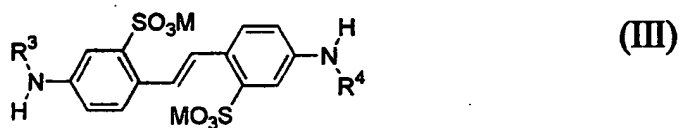
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in which M is hydrogen, an alkali metal atom (such as sodium or potassium) ammonium or a cation formed from an amine.

10

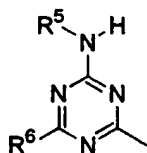
Another advantageous class of sunscreens which may be used with composition of the invention have a structure corresponding to formula (III):



15

wherein R³ and R⁴ are independently selected from groups of formula

- 8 -

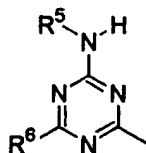


wherein each R⁵ and R⁶ is independently selected from phenyl, optionally substituted by one or more groups selected from iodo, nitro tertiary amino, and sulphonic acid (and salts thereof) groups, polyhydroxy straight or branched C₁₋₆ alkylene groups, N-di-C₁₋₄ alkylaminoalkyl, (N, N'-di-C₁₋₄ alkylaminoalkyl) amino and morpholino; and

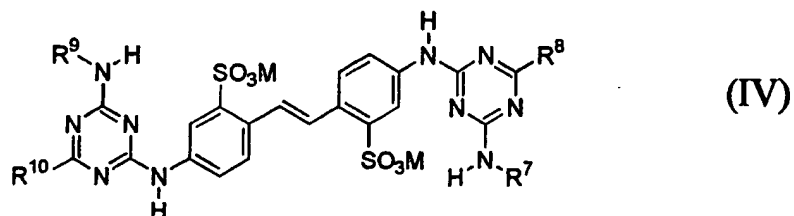
and naphthoyl benzoyl groups optionally substituted in the phenyl or naphthyl ring by one or more groups selected from iodo, nitro, tertiary amino and sulphonic acid (and salts thereof) groups; and

M is hydrogen, an alkali metal atom (such as sodium or potassium) ammonium or a cation formed from an amine

When R³ and R⁴ are both groups of formula

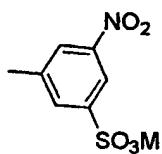
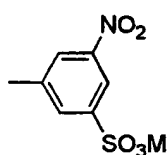
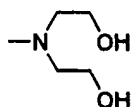


then the compound of formula (III) may for example have the formula

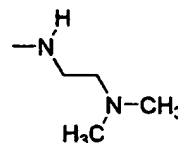
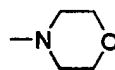
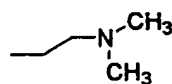


- 9 -

wherein

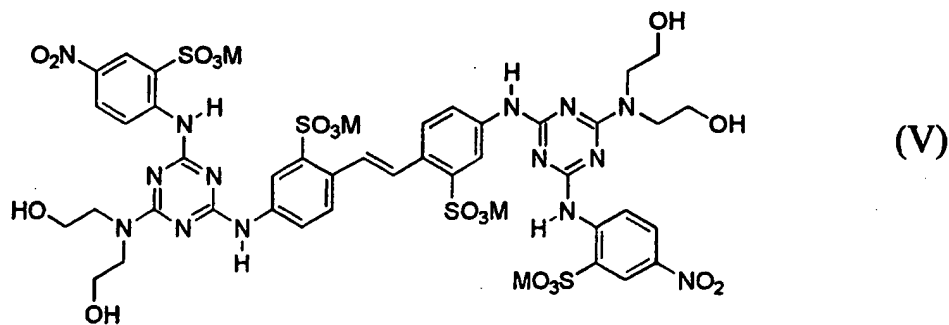
 R^9 may beand/or R^7 may beand/or R^{10} may be

or

and/or R^7 and R^9 may beand/or R^8 and R^{10} may beand/or R^7 , R^8 , R^9 and R^{10} may be

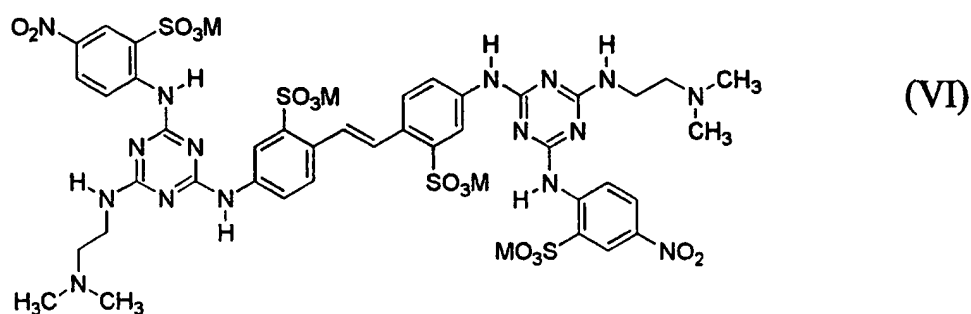
When R^3 and R^4 are both optionally substituted benzoyl, they may for example both be 4-nitrobenzoyl groups.

A preferred example of a compound of formula (III) is a compound of formula (V)



- 10 -

Another preferred example of a compound of formula (III) is a compound of formula (VI)



5 wherein, in formula (V) or formula (VI) is as hereinbefore defined.

Synthesis

10 Compounds of the classes of formulae (I) and (III) are non-fluorescing analogues of commercially available fluorsceners and therefore can be made by analogous synthetic routes as will be readily apparent to persons skilled in the art of synthetic organic chemistry.

Compositions

15 The present invention in another aspect, provides a detergent composition comprising surfactant material, optionally detergency builders, and may further optionally contain bleaching components and other active ingredients to enhance performance and/or physical properties.

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- 11 -

The level of sunscreen agent in such a composition may for example be from 0.01 wt% to 10 wt%, preferably from 0.025 wt% to 5 wt% of the total composition, more preferably from 0.05 wt% to 2.5wt%, e.g. from 0.075wt% to 2 wt%.

5 Detergent Active Compounds

The detergent compositions of the invention contain surfactant material which may be chosen from detergent active compounds selected from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

15 The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

20 The detergent compositions of the invention preferably contain an anionic surfactant. A preferred anionic surfactant is alkylbenzene sulphonate, particularly if they are linear alkylbenzene sulphonate, alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅ are especially preferred .

It is preferred if the level of anionic surfactant is from 5 wt% to 50 wt%, more preferably 10 wt% to 40 wt%, most preferably from 15 wt% to 35 wt%.

25 Other anionic surfactants suitable for use with the invention are well-known to those skilled in the art. Examples include primary and secondary alkyl sulphates, particularly C₈-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene

- 12 -

sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

The compositions of the invention may also contain nonionic surfactant.

5

It is preferable if the ratio of anionic surfactant to nonionic surfactant is equal to or greater than 2:3, more preferably greater than or equal to 3:2, most preferably equal to or greater than 4:1.

10

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₈-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants

15

include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

It is preferred if the level of nonionic surfactant is from 1 wt% to 35 wt%.

20

The choice of detergent-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

25

If a high foaming product is desired it is preferable to use nonionic surfactants that are not ethoxylated such as cocomonoethanolamide.

- 13 -

The total amount of surfactant present will also depend on the intended end use and may be as high as 60 wt%, for example, in a composition for washing fabrics by hand. In compositions for machine washing of fabrics, an amount of from 5 to 40 wt% is generally appropriate.

5

Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or nonionic surfactant, or combinations of the two in any ratio, optionally together with soap.

10

Detergency Builders

The detergent compositions of the invention will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

15

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB-A-1 437 950; crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB-A-1-473 201, amorphous aluminosilicates as disclosed in
20 GB-A-1 473 202 and mixed crystalline/amorphous aluminosilicates as disclosed in GB-A-1-470 250; and layered silicates as disclosed in EP-A-164 514B. Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

25

The detergent compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be

- 14 -

incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

5 The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:



10 These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

15 Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB-A-1 429 143. The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

20 The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P
25 type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

- 15 -

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

5 Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and
10 sulphonated fatty acid salts. This list is not intended to be exhaustive.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably
15 from 1 to 10 wt%.

Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

20 Bleach Components

Detergent compositions according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen
25 peroxide in aqueous solution.

- 16 -

Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

5

Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

10

The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%.

15

The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

20

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors caprolactam precursors and pernonanoic acid precursors. Especially preferred bleach precursor suitable for use in the present invention are N,N,N',N'-tetracetyl ethylenediamine (TAED) and sodium nonanoyloxybenzene sulphonate (SNOBS). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US-A-4 751 015 and US-A-4 818 426 and EP-A-402 971 are also of great interest. The cationic bleach precursors disclosed in EP-A-284 292 and EP-A-303 520 may also be used.

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- 17 -

The bleach system can be either supplemented with or replaced by a peroxyacid. Examples of such peracids can be found in US-A-4 686 063 and US-A-5 397 501. A preferred example is the imido peroxy-carboxylic class of peracids described in EP-A-325 288, EP-A-349 940, DE-A-382 3172 and EP-A-325 289. A particularly preferred example is phthalimido peroxy caproic acid (PAP). Also preferred are diperoxy carboxylic acids such as disclosed in EP-A-200 163, a particularly preferred example being diperoxy dodecanedioic acid (DPDDA). In general, any such peracids are suitably present at 0.1 - 12%, preferably 0.5 - 10%.

A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid). These Bleach stabilisers are also useful for stain removal, especially in products containing low levels of bleaching species or no bleaching species.

An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP-A-458 397, EP-A-458 398 and EP-A-509 787.

Enzymes

Enzymes are another preferred optional component of composition according to the present invention. Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

- 18 -

Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

5

Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins, which are obtained from particular strains of B. subtilis and B. licheniformis, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

10

Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark) (obtainable from Showa-Denko of Japan), Optimase (Trade Mark) (from Miles Kali-Chemie, Hannover, West Germany), and Suprase (Trade Mark) (obtainable from Pfizer of U.S.A.).

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20

Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%.

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- 19 -

Other ingredients

The compositions of the invention may optionally contain alkali metal, preferably sodium, carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate polymer, or sodium silicate.

One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; fabric softening compounds, soil release polymers, fluorescers and decoupling polymers. This list is not intended to be exhaustive.

The detergent composition when diluted in the wash liquor (during a typical wash cycle) will give a pH of the wash liquor from 7 to 10.5.

The detergent components of the present invention may be incorporated in detergent compositions of all physical types, for example, powders, liquids, gels and solid bars.

- 20 -

Detergent compositions of the invention may be prepared by any suitable method.

5 Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insensitive ingredients, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

10 Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/l, more preferably at least 500 g/l.

Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

15

Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower route (NTR) methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used.

Processes using high-speed mixer/granulators are disclosed, for example, in

20

EP-A-340 013, EP-A-367 339, EP-A-390 251 and EP-A-420 317.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention
25 can also be in compact form which means it will contain a lower level of water compared to a conventional liquid detergent.

- 21 -

EXAMPLES

The invention will now be illustrated by the following non-limiting examples. In the examples all percentages are expressed by weight.

5

Example 1: Spray-Dried Powder	wt%
Moisture	12.5%
Na LAS	23.6%
STPP	19.2%
Na silicate	4.8%
Sunscreen*	0.2%
SCMC	0.4%
Na Sulphate	28.6%
Calcite	10.3%
Minors	0.4%

- 22 -

Example 2:	wt%
NTR Granulated Powder	
Na LAS	10.4%
Non-ionic 7EO branched	5.5%
Non-ionic 3EO branched	2.9%
Soap	1.3%
Zeolite A24 (anhydrous)	35.4%
Na-citrate 2aq	7.8%
Light soda ash	7.0%
Sunscreen*	0.2%
SCMC	0.7%
Moisture, salts, NDOM	5.7%
Na-carbonate	11.4%
Na-bi-carbonate	4.0%
Minors	7.7%

*Examples 1A, 2A: The material of formula (II) as hereinbefore defined (as the Na salt)

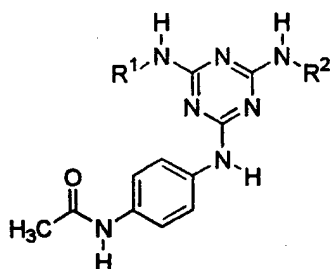
Examples 1B, 2B: The material of formula (V) as hereinbefore defined (as the Na salt)

Examples 1C, 2C: The material of formula (VI) as hereinbefore defined (as the Na salt)

- 23 -

CLAIMS:

1. A sunscreen agent which is a non-dye, substantially non-fluorescent, non-quaternary ammonium compound which absorbs UVA and/or UVB radiation wherein
5 at least 5%, preferably at least 7.5%, more preferably at least 10% by weight of the agent is deposited on a sheet of cotton-fabric immersed in a solution of 0.2 g/l of said agent in water for 1 hour at 21°C at a solution:sheet weight ratio of 25:1, (preferably followed by rinsing) and then followed by drying.
- 10 2. An agent according to claim 1, having a molar extinction coefficient of greater than $2000 \text{ mol}^{-1} \text{ cm}^{-1}$.
3. A sunscreen agent of formula (I)

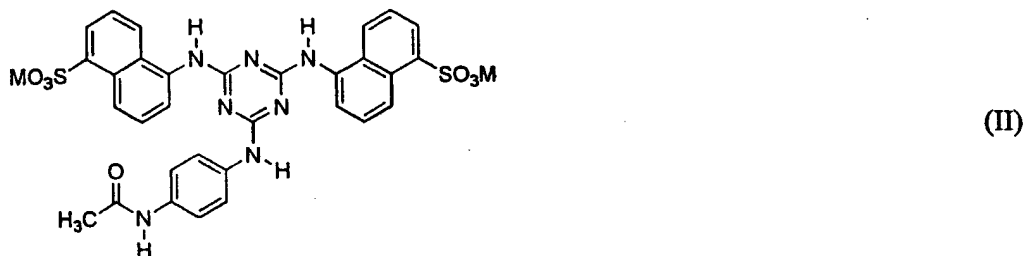


(I)

15 in which R¹ and R² are the same or different and are substantially flat planar groups which cause the molecule to absorb UVA and/or UVB, and have at least one water solubilising group.

- 24 -

4. A sunscreen of formula (II)



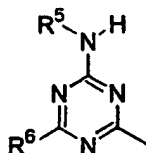
in which M is hydrogen, an alkali metal atom (such as sodium or potassium) ammonium or a cation formed from an amine.

5

5. A sunscreen agent of formula (III)



wherein R³ and R⁴ are independently selected from groups of formula



wherein each R⁵ and R⁶ is independently selected from phenyl, optionally substituted by one or more groups selected from nitro and sulphonic acid (and salts thereof) groups, polyhydroxy straight or branched C₁₋₆ alkylene groups, N-di-C₁₋₄ alkylaminoalkyl, (N, N'-di-C₁₋₄ alkylaminoalkyl) amino and morpholino; and

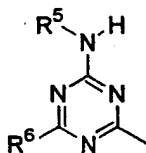
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- 25 -

benzoyl and naphthoyl groups optionally substituted in the phenyl or naphthyl ring(s) by one or more groups selected from iodo, nitro, tertiary amino and sulphonic acid (and salts thereof) groups; and

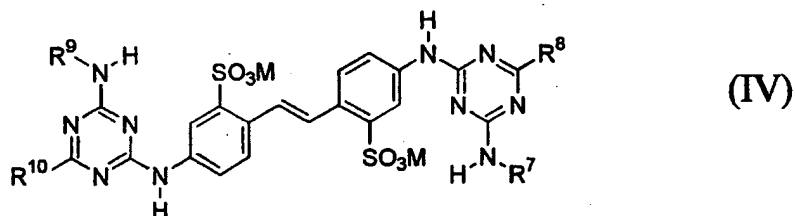
5 M is hydrogen, an alkali metal atom (such as sodium or potassium) ammonium or a cation formed from an amine.

6. A sunscreen agent according to claim 5, wherein when R^3 and R^4 are both groups of formula



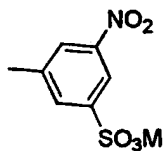
10

the compound of formula (I) has the formula

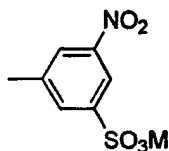


wherein

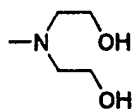
R^9 is



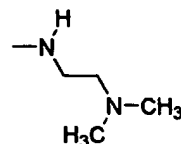
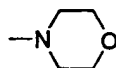
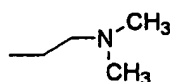
and/or R^7 is



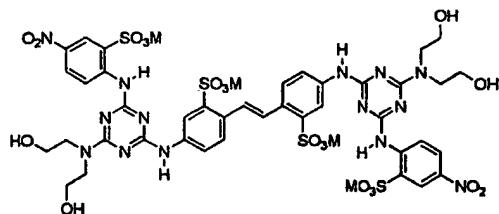
- 26 -

and/or R¹⁰ is

or

and/or R⁷ and R⁹ isand/or R⁸ and R¹⁰ isand/or R⁷, R⁸, R⁹ and R¹⁰ is

7. A sunscreen agent of formula (V)

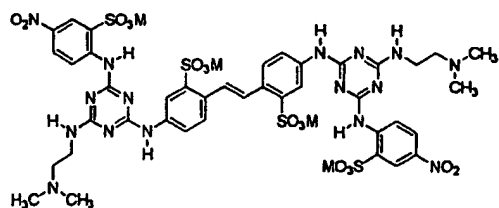


(V)

in which M is as defined in claim 5.

5

8. A sunscreen agent of formula (VI)



(VI)

wherein, M is as defined in claim 5.

- 27 -

9. A detergent composition comprising surfactant and an effective UV-inhibiting amount of a sunscreen agent according to any preceding claim.

5 10. A detergent composition according to claim 9, comprising from 0.01% to 10%, preferably from 0.025% to 5%, more preferably from 0.05% to 2.5% and most preferably from 0.075% to 2% by weight of sunscreen agent and from 5% to 40% by weight of surfactant.

INTERNATIONAL SEARCH REPORT

International Application No

PC/EP 99/01962

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C1103/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C110

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 728 749 A (CIBA-GEIGY) 28 August 1996 (1996-08-28) cited in the application claims 1-7, 24, 28, 29, 31 page 6, line 40-45 examples 7, 8, 21, 22 ----	1, 5-9
X	GB 2 291 644 A (CIBA-GEIGY) 31 January 1996 (1996-01-31) claims 1, 20-22, 25, 26, 28, 29 example 34 ----	1, 9
X	GB 2 291 658 A (CIBA-GEIGY) 31 January 1996 (1996-01-31) page 22, paragraphs 2, 4 examples 1-3 -----	1, 9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 September 1999

Date of mailing of the international search report

16/09/1999

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Authorized officer

Peeters, J

INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 99/01962

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-2, 9-10(all part.)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
See FURTHER INFORMATION SHEET PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-2 and 9-10 (all partially)

Present claims 1-2 relate to a sunscreen agent defined (inter alia) by reference to a number of physical parameters. The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the compounds structurally identified in the claims.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/01962

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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